

# Complex Quantum Phenomena in a Bilayered Calcium Ruthenate

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$\text{Ca}_3\text{Ru}_2\text{O}_7$  undergoes an antiferromagnetic transition at  $T_N = 56\text{K}$ , followed by a Mott-like (MI) transition at  $T_{\text{MI}} = 48\text{K}$ . This nonmetallic ground state, with a charge gap of  $0.1\text{eV}$ , is suppressed by a highly anisotropic metamagnetic transition that leads to a fully spin-polarized metallic state. We report the observation of Shubnikov-de Haas oscillations in the *gapped* state, colossal magnetoresistance in the inter-plane resistivity with a large anisotropy different from that observed in the magnetization, and non-Fermi liquid behavior in the metallic state at high magnetic fields.

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The colossal magnetoresistance (CMR) phenomenon, a gigantic decrease of resistance triggered by the application of a magnetic field, so far has only been observed in manganese[1] based oxides. Originally, this phenomenon was theoretically treated in terms of the double-exchange (DE) mechanism[2], whose basic description relies on the doping dependent valence states of Mn. However, to explain the richness of the experimentally observed phases, several instabilities, caused by a strong coupling between spin, charge and lattice degrees of freedom, have been proposed to compete with the ferromagnetic DE interaction. In fact, a series of experiments are explained[3] assuming that the manganites are intrinsically *inhomogeneous* and present strong tendencies toward phase separation between ferromagnetic metallic (FMM) and antiferromagnetic charge/orbital ordered insulating (AFI) domains.

This complex interplay between interactions, fluctuations, and inhomogeneities seems to be ubiquitous in transition metal oxides (TMOs). Although their description is still the subject of an intense debate, it is clear that most of these systems cannot be described by the standard Fermi liquid (FL) theory with interactions renormalized in Landau like quasiparticles. Only recently a stoichiometric[4] and an overdoped cuprate[5] have been claimed to present a FL-like ground state. In this respect, the 4d electron Ru-based stoichiometric oxides, or ruthenates, are perhaps unique systems since the oxygen vacancies inherent to the cuprates or the valence disorder peculiar to the manganites are *not* characteristics of these systems. In fact, in at least one compound,  $\text{Sr}_2\text{RuO}_4$ [6, 7] a FL ground state has been found. Despite the relative absence of disorder, the ruthenates are novel systems rich in complex physical phenomena as can be illustrated by the example of  $\text{Ca}_3\text{Ru}_2\text{O}_7$ [8, 9, 10]: With a double Ru-O layered orthorhombic structure[8],  $\text{Ca}_3\text{Ru}_2\text{O}_7$  (Ca327) belongs to the Ruddlesden-Popper series,  $\text{Ca}_{n+1}\text{Ru}_n\text{O}_{2n+1}$ , with  $n = 2$ , where  $n$  is the number of coupled Ru-O layers in a unit cell. Ca327 undergoes an antiferromagnetic ordering at  $T_N = 56\text{K}$  followed

by a sharp metal-nonmetal transition at  $T_{\text{MI}} = 48\text{K}$ [9] (throughout this manuscript we define a “non-metallic” regime whenever the slope of the resistivity respect to the temperature  $T$  is  $d\rho/dT < 0$ ). The inter-layer spacing, c-axis, collapses at  $T_{\text{MI}}$  [11] suggesting a strong coupling between the electrons and the lattice. In between  $T_N$  and  $T_{\text{MI}}$  the system is in an antiferromagnetic metallic state (AFM)[8, 9, 10], a rare occurrence for a stoichiometric compound at ambient pressure. At  $T < T_{\text{MI}}$  Ca327 undergoes a first-order metamagnetic (MM) transition for a  $B_{\text{MM}} \simeq 6\text{T}$  along the a-axis, which is responsible for negative magnetoresistive. In this field-induced ferromagnetic phase the spins are nearly completely polarized[8, 9]. At the MI transition, Raman spectra studies[12] reveal a rapid suppression of low-frequency electronic scattering closely associated with the formation of a charge gap  $\Delta_c \sim 0.1\text{eV}$ [12]. The corresponding gap ratio  $R = \Delta_c/k_B T_{\text{MI}} \sim 23$  is large, suggesting that this transition is driven by strong electronic correlations, typical of a Mott-Hubbard system [13, 14]. In addition, the optical conductivity at room temperature yields a large scattering rate,  $\hbar/2\tau = 0.84\text{eV}$ , corresponding to a very short mean free path  $\ell$ :  $0.8 \leq \ell \leq 8\text{\AA}$ . Remarkably, these values for  $\ell$ , assuming a typical Fermi velocity of  $10^7 - 10^8\text{cm/s}$  [15], are *well beyond* the so-called Mott-Ioffe-Regel limit for bandlike transport.

In this letter, we present an electrical transport study of the  $\text{Ca}_3\text{Ru}_2\text{O}_7$  compound at high magnetic fields ( $B$ ). At low temperatures, very low frequency Shubnikov-de Haas oscillations are observed for  $B$  nearly parallel to the c-axis *only* in the “insulating” state. Consequently, Ca327 exhibits the *coexistence* of quasiparticles with a “gapped” ground state. Below  $T_{\text{MI}} = 48\text{K}$ , and for an angle dependent critical field in the b-c plane, a phase transition suppresses this gapped state stabilizing a ferromagnetic metallic phase. At the transition, colossal like negative magnetoresistance, assisted perhaps by a spin-valve type effect, is observed in the inter-layer resistivity  $\rho_c$ , what leads to a resistivity drop by a factor

FIG. 1: (a) Inter-plane resistivity  $\rho_c$  of a  $\text{Ca}_3\text{Ru}_2\text{O}_7$  single crystal as a function of magnetic field  $B$  and for several temperatures  $T$ . Inset:  $\rho_c$  as a function of  $B$  in a limited range and for  $T = 20$  mK. Notice the development of an oscillatory component as  $T$  is lowered. (b) The amplitude of the SdH oscillations as a function of  $B^{-1}$  for several temperatures. Solid lines are a guide to eyes. Inset: SdH amplitude normalized respect to the temperature  $T$  and as a function of  $T$ . Solid line is a fit to LK formulae.

reconstruction at  $T_{\text{MI}}$ , due, for instance, to an eventual spin/orbital ordering: A gap opens along most of the FS leaving (very) small-reconstructed electron and/or hole FS pockets. This would be consistent with the small value of  $\mu_c$ , i.e., a small density of states, indicating a small amount of charge carriers at the Fermi level. In fact, orbital ordering is predicted to occur in  $\text{Ca}_2\text{RuO}_4$  [18], compatible with a sudden change in the basal plane at  $T = 357$  K [19, 20]. But for  $\text{Ca}_3\text{Ru}_2\text{O}_7$ , besides the collapse of the c-axis, no firm evidence for orbital ordering has been reported so far. At high fields the absence of QOs, or any other indication of FL behavior in the FMM state, clearly indicates the relevance of the electron correlations for this system.

QOs are detected when  $B$  is relatively close to the c-axis, but when  $B$  is tilted towards the a or the b-axis we observe an orientation-dependent metamagnetic transition. For fields along the a-axis, a very sharp first or-

FIG. 2: (a) Inter-plane resistivity  $\rho_c$  of a  $\text{Ca}_3\text{Ru}_2\text{O}_7$  single crystal (sample # 1) as a function of magnetic field  $B$  along both the a and the b-axis at  $T = 0.6$  K. (b)  $\rho_c$  from a second sample (sample # 2) as a function of  $B$  at  $T = 0.6$  K and for several angles  $\theta$  in the b-c plane. The step in angle between traces is  $\Delta\theta \simeq 7^\circ$ . Lower panel:  $\rho_c$  as a function of  $T$  for two values of  $B$ , 0 and 30 T along the b-axis. Notice, how the gapped state is entirely suppressed by the field. Inset:  $\rho_c$  as a function of  $T^{1.2}$  for  $B = 30$  T along the b-axis. Notice the linear dependence.

most relevant fact is the rather *anisotropic* field-induced suppression of the charge gapped state. Similar but isotropic behavior is observed in the  $\text{RE}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  (RE= Pr, Nd, Sm,...) compounds[22], where the commensuration of the band filling (doping level) with the crystal lattice spacing is believed to be responsible for their orbital/charge ordered ground state. The application of a field produces a remarkable decrease in resistivity at a MM transition where a FM metallic phase is stabilized at the expense of the charge/orbital ordered (OO) state. From a thermodynamic point of view, this field-induced “melting” of the OO phase is understood by assuming that both states are *almost* degenerate in energy, but under an external field  $H$  the free energy of the FM metallic state may become lower due to the Zeeman term  $-M_s H$  ( $M_s$  is the spontaneous magnetization) inducing the hysteretic structural transition seen

FIG. 3: Upper panel:  $\rho_c$  as a function of  $B$  parallel to the b-axis and for several temperatures  $T$ . The MM transition moves towards lower  $B$  as  $T$  increases. Lower panel: The resulting  $B - T$  phase diagram of  $\text{Ca}_3\text{Ru}_2\text{O}_7$ . At low fields, and as the  $T$  is lowered, it shows two successive transitions, an antiferromagnetic metallic (AF-M) phase, followed by a gapped ground state, where the Ru-O planes seem to order in an antiferromagnetic A-type phase (AFM-NM). For  $B \parallel$  a-axis, the AFM-NM phase is suppressed by a sharp MM transition at  $B_{\text{MM}} \leq 6$  T (indicated by solid circles), which leads the system into a ferromagnetic poorly metallic phase (FM-M(I)). For  $B \parallel$  b-axis, the MM transition at  $6 \leq B_{\text{MM}} \leq 15$  T completely “melts” the charge gap associated to the AFM-NM phase (opened circles), leading to a ferromagnetic metallic phase (FM-M(II)). The CMR effect is seen at the MM transition. Although the spins are nearly completely polarized along  $B$ , the FM-M(II) phase still shows an anomalously high resistivity and a nearly linear dependence on  $T$  characteristic of a non-FL (gray area). At low  $T$  and for  $B \parallel$  b-axis, QOs are observed *only* in the AFM-NM phase. At higher  $T$ , open squares show the frontier between the antiferromagnetic metallic (AFM-M) phase and, both, the paramagnetic metallic (PM-M) and the FM-M(II) phases.

experimentally[1]. It is interesting to mention that OO in the  $t_{2g}$  orbitals is predicted to occur in ruthenates[18], and it has in fact, been reported in  $\text{Ca}_2\text{RuO}_4$ [20]. In this framework, the gapped state of  $\text{Ca}_3\text{Ru}_2\text{O}_7$  could perhaps be the result of an OO transition at  $T_{\text{MI}}$  while the CMR effect would result from an eventual field-induced OO melting transition. This intriguing hypothesis certainly deserves further studies. Similarly to the bilayered  $\text{Ca}_3\text{Ru}_2\text{O}_7$ , anisotropic CMR[23] and spin-valve like effects [24, 25] have already been reported in bilayered manganites. Although we unveil here similarities between both families,

the QOs and the highly anisotropic, doping independent, CMR like effect seen in  $\text{Ca}_3\text{Ru}_2\text{O}_7$  suggest that the physics of the ruthenates is indeed unique. Alternatively, their study is a promising new route for exploring the physics of CMR systems.

In summary, we have shown clear evidence for Landau quasiparticles coexisting with a gapped ground state in a transition metal oxide. Furthermore, our study reveals that Ru based oxides can also display colossal magnetoresistance like behavior.

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